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SYNTHESIS AND π-AMPHOTERIC PROPERTIES OF TRIS(TETRATHIAFULVALENO)HEXADEHYDRO[12]ANNULENE

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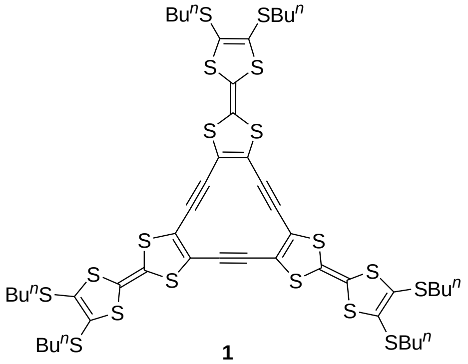
Abstract – The Sonogashira coupling reaction of the diiodide **6** of 1,2-[4,5-bis(butylthio)tetrathiafulvalenyl]ethyne with 4,5-bis(ethynyl)-4',5'-bis-(butylthio)tetrathiafulvanene **5** produced the corresponding tris(tetrathiafulvaleno)hexadehydro[12]annulene **1** in moderate yield. The [12]annulene **1** exhibits multi-redox behavior and solvatochromism in the neutral state.

INTRODUCTION

Hexadehydro[12]annulene has received considerable attention, because its tribenzo-analogue is regarded as a structural unit of graphyne,[1] and because various unique transition-metal complexes have been constructed using the [12]annulene frame.[2,3] Furthermore, tribenzohexadehydro[12]annulene (TBA) has been employed as a starting material for the synthesis of cage molecules and polyethers.[4,5] Recently, we have reported the synthesis and π-amphoteric properties of bis(tetrathiafulvaleno)hexadehydro[12]-annulene **2** and related compounds based on the tetrathiafulvalene (TTF) and [12]annulene moieties.[6,7] The annulene **2** exhibited multi-redox potentials, solvatochromism, and the formation of a large sandwich complex. Based on these results, we next synthesized tris(tetrathiafulvaleno)hexadehydro[12]annulene **1**. We report here the synthesis, unique redox behavior, and solvatochromic properties of **1**.

RESULTS AND DISCUSSION

The synthesis of **1** is summarized in Scheme 1. Although various synthetic methods of accessing hexadehydro[12]annulenes have been reported to date,[8,9] we employed the Sonogashira coupling of the bis(ethynyl)-TTF **5** with the diiodo-bi-TTF **6** similar to our previously reported procedure[6] owing to the instability of **1** to light, atmospheric oxygen, and acidic condition. Thus, the reaction of the diiodo-TTF **3** with trimethylsilylacetylene (4 equiv) in the presence of $Pd(PPh_3)_4$ (15 mol%), CuI (30 mol%), and Et_3N



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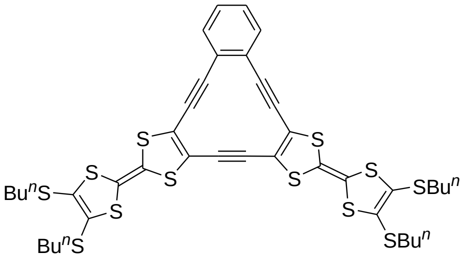

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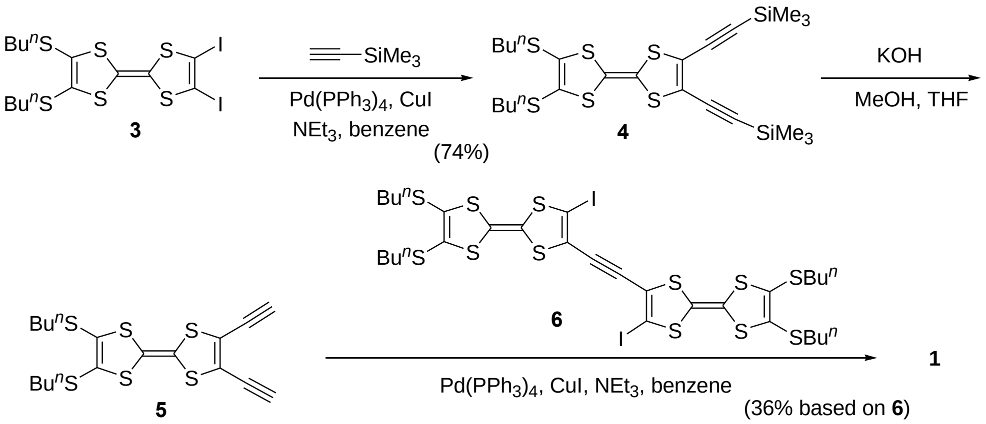
in benzene at 50 °C for 12 h produced the bis(trimethylsilylethynyl)-TTF **4** in 74% yield. The treatment of **4** with KOH (excess) in THF-methanol (1:1) at room temperature for 3 min yielded **5** to remove the trimethylsilyl groups. Since **5** was unstable and readily polymerized after removal of the solvent, a solution of **5** in benzene was employed for the following reaction without further purification. The Sonogashira coupling of **6** with **5** (1.65 equiv based on 100% conversion of **4**) in the presence of $Pd(PPh_3)_4$ (50 mol%) and CuI (100 mol%) in benzene-triethylamine (10:3) at room temperature for 5 h produced the desired **1** in 36% yield based on **6**.[10] For the synthesis of **1**, almost stoichiometric amounts of $Pd(PPh_3)_4$ and CuI were required to complete the reaction.



Scheme 1. Synthesis of tris(TTF)[12]annulene **1**

Interestingly, the tris(TTF)annulene **1** shows solvatochromism, and a solution of **1** is deep green in CS_2 but bright green in CH_2Cl_2. As shown in Figure 1, the UV-Vis-NIR spectrum of **1** shows strong (322 nm, $\varepsilon = 90{,}000$) and weak (623-656 nm, $\varepsilon = 3500$-4000) absorptions. The strong absorption is unchanged with the type of solvent, whereas the weak absorption varies with the type of solvent used [λ_{max} (CS_2) 656 nm and λ_{max} (CH_2Cl_2) 623 nm]. Since the longest absorption is assigned to the charge-transfer (CT) band from the TTF (π-donor) to [12]annulene (π-acceptor) moieties, this transition is sensitive to the polarity of the solvent.

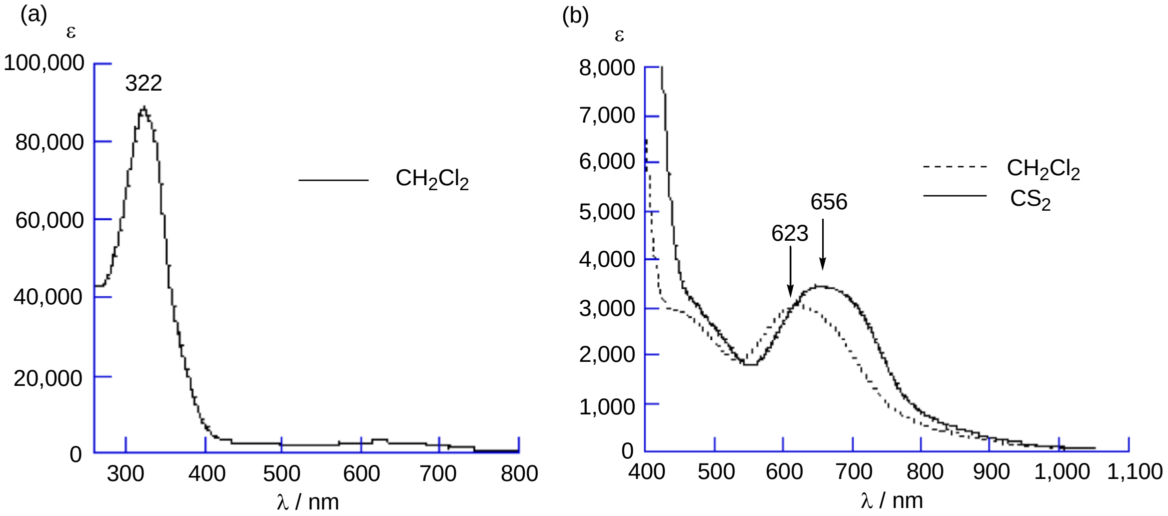


Figure 1. UV-Vis-NIR spectra of **1**. (a) Entire spectrum in CH_2Cl_2. (b) Expansion of the weak absorptions in CH_2Cl_2 and CS_2.

The cyclic voltammetric (CV) analysis of **1** shows unique redox properties owing to the π-amphoteric nature of **1**. As shown in Table 1, **1** and **2** indicated 4-step redox processes; namely, the formation of $\mathbf{1}^{2-}$, $\mathbf{1}^{-}$, $\mathbf{1}^{3+}$, and $\mathbf{1}^{6+}$, or $\mathbf{2}^{2-,}$ $\mathbf{2}^{-}$, $\mathbf{2}^{2+}$, and $\mathbf{2}^{4+}$. Since tribenzohexadehydro[12]annulene (TBA) shows two reduction waves at -2.50 and -2.19 V vs Fc/Fc^+ under the same conditions, the reduction potential of the [12]annulene unit increases in the order **1** > **2** > TBA, reflecting the increase in the degree of cyclic conjugation.[11] In contrast, the oxidation potentials of **1** and **2** seemed to be similar. However, the first oxidation potential of **1** was split into two ($E^{ox1}_{1/2}(1)$ = 0.12 V; $E^{ox1}_{1/2}(2)$ = 0.26 V vs Fc/Fc^+) when measured at a very slow rate (3 mV s^{-1}), while the first oxidation potential of **2** showed a broad oxidation even when measured at a very low rate.[12] Consequently, the oxidation potential of the TTF units decreases in the order **2** ≥ **1** > TTF, reflecting the increase in donor ability.

Table 1. Redox potentials of **1**, **2**, and TTF vs Fc/Fc^+ at room temperature.[a]

Compound	$E^{red2}_{1/2}$	$E^{red1}_{1/2}$	$E^{ox1}_{1/2}$	$E^{ox2}_{1/2}$
TTF	—	—	-0.08	0.30
1	-1.78	-1.41	0.21 (0.12, 0.26)[b]	0.49
2	-1.87	-1.50	0.19	0.46

[a] Reduction potential was measured in THF using $^{n}Bu_4NClO_4$ (0.1 M), glassy carbon (working electrode), Pt (counter electrode), and 100 mVs^{-1}, whereas oxidation potential was measured in benzonitrile using $^{n}Bu_4NClO_4$ (0.1 M), Pt (working and counter electrodes) and 100 mV s^{-1}. The potential was measured against a Ag/Ag^+ reference electrode and converted to the value vs Fc/Fc^+.
[b] Measured at 3 mV s^{-1}.

The CV analysis of **1** showed three oxidation potentials (Table 1). Accordingly, the chemical oxidation of **1** with $Fe(ClO_4)_3$ revealed characteristic changes in color and electronic spectra.[13] As shown in Figure 2, the oxidation of **1** with 1, 2, 3, and 6 equiv of $Fe(ClO_4)_3$ in CH_2Cl_2–CH_3CN (v/v 4:1) resulted in the formation of $\mathbf{1}^{+\cdot}$ (859 and ca. 2000 nm), $\mathbf{1}^{2+}$ (872 nm), $\mathbf{1}^{3+}$ (860 nm), and $\mathbf{1}^{6+}$ (694 nm), respectively. The solutions changed from green (**1**) to dark orange ($\mathbf{1}^{+\cdot}$), greenish orange ($\mathbf{1}^{2+}$), dark green ($\mathbf{1}^{3+}$), and blue ($\mathbf{1}^{6+}$). The cation radical $\mathbf{1}^{+\cdot}$ shows a very broad absorption at approximately 2000 nm probably owing to the strong intermolecular interaction between the TTF and $TTF^{+\cdot}$ units. However, the possible formation of a mixed valence dimer ($\mathbf{1}_2^{3+}$) was ruled out, because $\mathbf{1}_2^{3+}$ (*i.e.*, $\mathbf{1}^{1.5+}$ in Figure 2)[14] exhibited a weak absorption at approximately 2000 nm as shown in Figure 2. Regarding $\mathbf{1}^{3+}$, no π-dimer formation was observed based on its electronic spectra, and the absorption of $\mathbf{1}^{3+}$ (860 nm) appeared almost the same as that of $\mathbf{1}^{+\cdot}$ (859 nm).[15] However, the absorption of $\mathbf{1}^{2+}$ (872 nm) showed a red shift corresponding to the intramolecular head-to-tail interaction of two $TTF^{+\cdot}$ units.[16] In contrast to the preferable π-dimer formation of tris(TTF)[18]annulene trications,[17] the absence of the π-dimer formation of $\mathbf{1}^{3+}$ might have been due to the difficulty in stacking the [4n] π-electron system.[18]

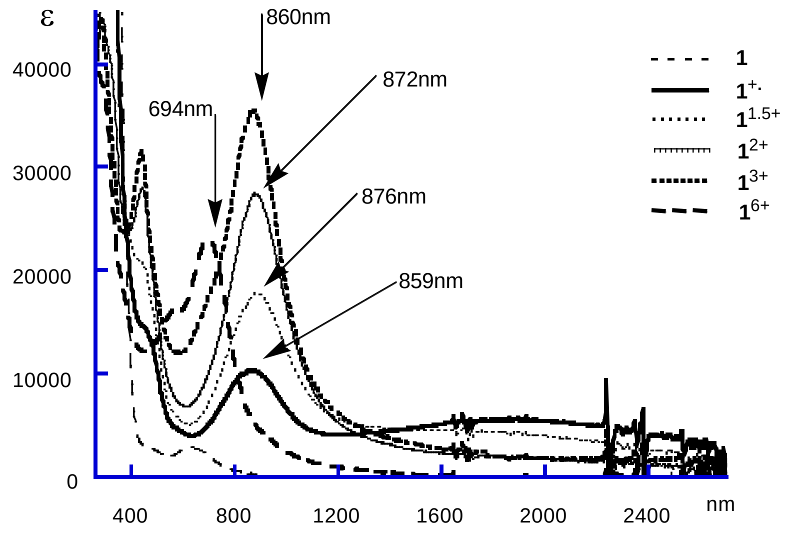


Figure 2. UV-Vis-NIR spectra of cationic species derived from **1** in CH_2Cl_2–CH_3CN (4:1)

In summary, the synthesis of the tris(TTF)[12]annulene **1** was successfully carried out using the nearly stoichiometric Sonogashira coupling of the diiodo-biTTF **6** with the diethynyl-TTF **5**. The TTF-annulene **1** exhibits solvatochromism, electrochromism, and multi-redox behavior owing to the π-amphoteric nature of **1**. Although **1** is unstable in the solid state, presumably owing to the combination of the [4n] π-electron system with π-donors, the introduction of electron-withdrawing groups into the TTF units in **1** can stabilize the molecule.

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10. Data for **1**: dark green powder, mp (measured by DSC) 91.2 ºC (decomp.); LDI-MS *m/z* 1206 (M^+); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.78 (t, *J* = 7.4 Hz, 12H), 1.59 (quint, *J* = 7.4 Hz, 12H), 1.42 (sext, *J* = 7.4 Hz, 12H), 0.93 (t, *J* = 7.4 Hz, 18H); ^{13}C-NMR (125MHz, $CDCl_3$) δ 13.6, 21.6, 29.7, 36.1, 92.9, 106.7, 114.4, 123.2, 127.8; UV-Vis (CH_2Cl_2, ε) 322 (90000), 623 (3800) nm. Anal. Calcd for $C_{48}H_{54}S_{18}$: C, 47.72; H, 4.51. Found: C, 47.61; H, 4.58.

11. Since the double bonds of TTFs have an olefinic character, the [12]annulene ring in **1** is more paratropic than that in **2**. Similarly, the paratropicity of **2** is much more stronger than that of tribenzohexadehydro[12]annulene (TBA). Therefore, the first reduction potential of the [12]annulene unit increases in the order TBA < **2** < **1**, reflecting the increase in the degree of cyclic conjugation. The LUMO levels of **1**, **2**, and TBA are **1** < **2** < TBA, reflecting the decrease in the degree of cyclic conjugation, see: M. Iyoda, Y. Onishi, and M. Nakagawa, *Tetrahedron Lett.*, 1981, **22**, 3645.

12. The CV analysis of **1** and **2** in benzonitrile at room temperature revealed that these compounds show only weak intra- and intermolecular interactions in the cationic states, although some TTF oligomers show fairly strong intra- and intermolecular interactions owing to mixed valence dimer and π-dimer formations.[7a]

13. For the chemical oxidation of TTFs with $Fe(ClO_4)_3$, see: M. Iyoda, M. Hasegawa, Y. Kuwatani, H. Nishikawa, K. Fukami, S. Nagase, and G. Yamamoto, *Chem Lett.*, 2001, 1146.

14. The oxidation of **1** with 1.5 equiv of $Fe(ClO_4)_3$ in CH_2Cl_2–CH_3CN (v/v 4:1) resulted in the formal formation of $\mathbf{1}^{1.5+}$ as shown in Figure 2. Although the formation of a mixed valence dimer ($\mathbf{1}_2{}^{3+}$) was expected, the electronic spectrum of $\mathbf{1}^{1.5+}$ showed only a weak absorption at *ca.* 2000 nm and hence almost no formation of a mixed valence dimer ($\mathbf{1}_2{}^{3+}$) in solution. For the formation of a mixed valence dimer from the tris-TTF system, see: M. Hasegawa, J. Takano, H. Enozawa, Y. Kuwatani, and M. Iyoda, *Tetrahedron Lett.*, 2004, **45**, 4109.

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16. The intramolecular head-to-tail (or side-by-side) interaction of the two cation-radicals shows a bathochromic shift of the longest absorption maximum owing to Davydov red shift,[19] see:

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